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(21) International Application Number: PCT/AU96/00284 (22) International Filing Date: 9 May 1996 (09.05.96) (30) Priority Data: PN 2911 10 May 1995 (10.05.95) AU (71) Applicant (for all designated States except US): JAMES HARDIE RESEARCH PTY. LIMITED [AU/AU]; 65 York Street, Sydney, NSW 2000 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): WILLIAMS, Peter, Allan [AU/AU]; 3 Savoy Court West, West Pennant Hills, NSW 2125 (AU). DENNIS, Gary, Ralph [AU/AU]; 23 Emma Parade, Winmalee, NSW 2777 (AU). JOSHUA, Nilmini, Sureka [AU/AU]; 106 John Terbutt Place, Richmond, NSW 2753 (AU). SLOANE, Brian, Patrick [AU/AU]; 14 Nottingham Street, Old Toongabbie, NSW 2146 (AU). (74) Agent: SHELSTON WATERS; 60 Margaret Street, Sydney, NSW 2000 (AU).			(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: A METHOD OF SLOWING THE SETTING RATE OF MAGNESIUM PHOSPHATE CEMENTS			
(57) Abstract A method for slowing the setting rate of a magnesium phosphate cement comprising adding a suitable base to an uncured or partially cured aqueous mix of the magnesium phosphate cement in an amount sufficient to raise the pH and minimise MgO/Mg(OH) ₂ dissolution. Suitable magnesium phosphate cements include ammonium magnesium phosphate cements and potassium magnesium phosphate cements.			

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A METHOD OF SLOWING THE SETTING RATE OF MAGNESIUM PHOSPHATE CEMENTS

FIELD OF THE INVENTION

This invention relates to a method of slowing the setting rate of hydrated
5 cements.

BACKGROUND OF THE INVENTION

The most commonly used hydrated cement is portland cement formed by
burning a mixture of clay and limestone. In some applications portland cement has
properties that render it less than ideal. These include situations where the cement is
10 required to be rapid setting or in which the product concerned is likely to be exposed
to high temperatures. Additionally, when cured concrete made from ordinary portland
cement is subjected to carbonation due to atmospheric carbon dioxide exposure the
alkaline cement reaction products carbonate to calcium carbonate reducing its
alkalinity and eventually causing micro-cracking of the concrete. This leads to
15 corrosion of reinforcing steel where there is inadequate concrete cover over the steel.

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The use of magnesium ammonium phosphate ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$), commonly known as struvite, as a hydrated cement is well documented. This compound occurs as a natural mineral or may be synthesised. Known magnesium ammonium phosphate cements have an initial setting time of about 1 to 5 minutes.

5 This time is too short in many specialised applications such as fabrication and it would be desirable to slow the setting time down. Previous methods to slow down the setting time have involved the addition of borax or halides (such as sodium chloride or barium salts) as setting rate retardants. Borax has disadvantages including in that it is very soluble in water and in order to slow the setting time, a substantial amount of

10 borax must be added with consequent loss of strength of the final product. Halides are also not desired setting retardants. Chlorides in general are not desirable additives since materials containing them are liable to give off hydrogen chloride gas at high temperatures and their retarding effects occurring within a couple of minutes is not very significant. Barium salts are not desirable in view of cost and toxicity problems.

15 Magnesium ammonium phosphate cements have the additional disadvantage of inadequate mechanical properties and moisture resistance compared to portland cement for general purpose use. Despite the problems struvite cements have been used in applications requiring rapid set times such as the repair of cracks in concrete roads and have also been used in the manufacture of furnace lining boards.

20 OBJECT OF THE INVENTION

It is an object of this invention to substantially ameliorate at least some of the disadvantages of the prior art.

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DISCLOSURE OF THE INVENTION

In a first aspect, this invention consists in a method for slowing the setting rate of a magnesium phosphate cement comprising adding a suitable base to an uncured or partially cured aqueous mix of the magnesium phosphate cement in an amount sufficient to raise the pH and minimise $\text{MgO}/\text{Mg}(\text{OH})_2$ dissolution.

In another aspect, the invention consists in a cementitious article formed using the method of the first aspect.

PREFERRED EMBODIMENTS OF THE INVENTION

Suitable magnesium phosphate cements include ammonium magnesium phosphate cements and potassium magnesium phosphate cements ($\text{MgKPO}_4 \cdot n\text{H}_2\text{O}$). The cement is chosen depending on its end application.

When the magnesium phosphate cement is ammonium magnesium phosphate, a suitable base is ammonia. Preferably, in order to prepare the cement, the ammonia is added to mono ammonium phosphate to which magnesium oxide is subsequently added. Preferably the ratio of ammonia to phosphate is 0.5-2.0:1, most preferably 1:1 and the ratio of magnesium to phosphate is 7-1:1, most preferably 3:1. Ratios of ammonia to phosphate above 2:1 tend to produce crumbly cements.

When the magnesium phosphate cement is a potassium magnesium phosphate cement, a suitable base is potassium hydroxide or potassium carbonate. Similarly in order to prepare the cement the base is preferably added to mono ammonium phosphate prior to the addition of magnesium oxide. Preferably the ratio of potassium to phosphate is 0.5-2.0:1, most preferably 1:1 and the ratio of magnesium to phosphate is 7-1:1, most preferably 3:1. Ratios of magnesium to

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phosphate greater than 7:1 tend to result in cements having reduced setting times and increased viscosity and are generally unworkable.

In a preferred aspect, the invention consists in a method of slowing the setting rate of an ammonium magnesium phosphate cement comprising the steps of reacting
5 ammonia with an ammonium phosphate compound in the presence of water and subsequently reacting the mixture with a magnesium compound to form a compound having the formula $\text{NH}_4\text{MgPO}_4 \cdot n\text{H}_2\text{O}$, wherein the amount of ammonia used is sufficient to raise the pH and minimise $\text{MgO}/\text{Mg}(\text{OH})_2$ dissolution.

In another preferred aspect, the invention consists in a method of slowing the
10 setting rate of potassium magnesium phosphate cement comprising the steps of reacting an ammonium phosphate compound with a potassium compound in the presence of water and subsequently reacting the mixture with a magnesium compound to form a compound having the formula:



15 wherein the amount of potassium compound used is sufficient to raise the pH and minimise $\text{MgO}/\text{Mg}(\text{OH})_2$ dissolution.

It is found by adding the potassium compound to the ammonium phosphate compound prior to addition of magnesium oxide that the rate of set is slowed to such an extent that the cement is suitable for fabrication.

20 The ammonium phosphate compound is preferably mono ammonium phosphate, the potassium compound is preferably potassium carbonate and the magnesium compound is preferably magnesium oxide. It will be apparent, however,

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that other materials may be used as the source of phosphate, potassium and magnesium.

The setting time of the hydrated cement according to this invention can be controlled by adjusting the pH of the cement at the time of setting. Preferably the pH is raised to a value between 4 to 10, more preferably to a value between 8 and 9. For potassium magnesium phosphate cements, the pH is preferably controlled by using potassium carbonate or potassium hydroxide as a source of potassium in the preparation of the compound. Preferably potassium carbonate is used as it has some buffering effect. It has also been found that the setting time of the hydrated cement may be further delayed by the gradual addition of excess water to the final mixture or by mechanical agitation and working of the mix.

Although there is no limit on the amount of water used in order to maximise strength, it is desirable to use only a slight excess from that stoichiometrically required to form the desired hydrated cement so as to form a smooth paste before setting. Once the cement has started to set any amount of water can be added to slow the setting time with either none or minimal loss of strength.

The hydrated cement prepared by the method of the invention can additionally contain density modifiers such as flyash, expanded polystyrene beads, cenospheres, vermiculite, perlite or predigested calcium silicate hydrate. Other additives can include fibre reinforcements such as cellulose, glass, polymer or wollastonite fibres.

The hydrated cement can be prepared as a foam cement.

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The magnesium potassium phosphate cement prepared by the method of this invention has been found to have a high strength at ambient temperature, to retain shape without distortion at high temperatures, exhibit low shrinkage at high temperatures, to have low water permeability and is crystalline in appearance.

5 The hydrated cement prepared according to this invention may be readily formed from commercially available raw materials and a high degree of purity is not required for reliable manufacture of the product.

The invention will now be described, by way of example only, with reference to specific examples.

10 The hydrated cement prepared according to this invention may be formed, for example, in a conventional concrete mixer using the following method:-

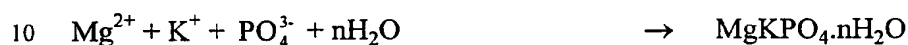
- (1) Dry mono ammonium phosphate $\text{NH}_4\text{H}_2\text{PO}_4$ is mixed with potassium carbonate K_2CO_3 in approximately stoichiometric quantities and a controlled amount of water added.
- 15 (2) Magnesium oxide is then added to these materials and a further controlled amount of water added. The cement will now react and set.
- (3) The setting time may be further delayed by the addition of yet more water to the mixture which displays thixotropic properties during the setting process.

 The method can form cements with various levels of hydration in terms of
20 water molecules bound to the compound. If no excess water is added then when the compound sets, there is no surplus water to cause drying shrinkage, the cement has a very low porosity, and there is no need to dry excess water from articles formed from the cement.

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For a rapid or slightly delayed set, minimal quantities of water are added, forming cements with the minimal quantities of bound water. For a further delayed set larger quantities of water are added, forming compounds up to the maximum level of bound water.

- 5 For magnesium potassium phosphate cements the chemical reactions which occur can be represented as follows:-



- Although the above reactions are depicted around mono ammonium phosphate as the source of phosphate, potassium carbonate as the source potassium and the method of controlling the pH and consequently setting time, and magnesium oxide as the source of magnesium, other materials may be used or the materials may be used in other combinations.
- 15

A typical formulation for preparing a magnesium potassium cement according to the method of the invention is:-

	$\text{NH}_4\text{H}_2\text{PO}_4$	42 kilograms
	K_2CO_3	25 kilograms
20	MgO	45 kilograms
	H_2O	20 litres (minimum) or an amount adjusted to suit

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The mole ratio of $K_2CO_3:NH_4H_2PO_4:MgO:H_2O$ is suitably 1:2:6:6. Using such a mole ratio the pH is raised from a pH of 4 to 5 (corresponding to the pH of a saturated solution of $NH_4H_2PO_4$) to a pH of 8 to 9.

The purity of the raw materials is not crucial to the formation of the cement
5 and the normal commercial purity of bulk commodity raw materials is of sufficient quality for reliable manufacture of this invention. The batching accuracy of the raw materials is not critical to the formation of the cement and normal site mortar mixing accuracy of around 10% is adequate. The dry raw materials can be pre-packaged in approximately stoichiometric quantities. For potassium magnesium phosphate
10 cements a two component hydrated cement mix can be provided comprising a first component containing a mixture of mono ammonium phosphate and potassium carbonate and a second component containing magnesium oxide. Accurate addition of water can be achieved by use of a meter or fixed volume containers.

Using commercially available grades of the raw materials cured magnesium
15 potassium phosphate cement made in accordance with the above typical formulation, has been found to exhibit strengths of about 50% of that obtained from cured specimens of ordinary portland cement and to exhibit a pore structure which is relatively impermeable to water. The linear shrinkage of cured magnesium potassium phosphate cement specimens subjected by heating to temperatures of about 1000°C
20 then cooling in a dessicator has been measured to be about 2% of the original length. No distortion is evident in such specimens.

The pH of the cured magnesium potassium phosphate cement is suitably alkaline such that reinforcing steel bound by concrete formed from the cement will be

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passivated and therefore not subject to corrosion, and the permeability of the cement is such that the ingress of water to corrode the steel is inhibited. Additionally, cured magnesium potassium phosphate cement is not subject to any known reaction with atmospheric carbon dioxide in the same way as ordinary portland cement. Thus

5 concrete formed using the cement of this invention is expected to be dimensionally stable with age and to maintain its non corrosive features to reinforcing steel indefinitely.

The applications of the cement according to this invention include:-

- a raw material in the manufacture of refractory materials;
- 10 a binding cement in the installation of refractory materials;
- a binding cement in structural concrete;
- a binding cement in extruded and pressed mortar articles;
- a binding cement for fibre reinforced articles such as those containing fibres including cellulose, glass, wollastonite and/or polymers; and
- 15 a rapid setting concrete for use in marine environments.

Example 1 - Retarding an ammonium magnesium phosphate cement containing flyash.

The formulation used in this Example was as follows:

	concentrated aqueous ammonia (25%)	23mls
20	mono ammonium phosphate	36g
	flyash	25g
	magnesium oxide	38g
	and water	14mls

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This formulation corresponds to a mole ratio of $\text{NH}_3:\text{NH}_4\text{H}_2\text{PO}_4:\text{MgO}:\text{H}_2\text{O}$ of 1.0:1.0:3.0:5.3.

The mono ammonium phosphate, ammonia and water were first mixed together thoroughly, the flyash was then blended into the mixture and magnesium
5 oxide was then added resulting in a hexahydrated ammonium phosphate cement.

Example 2 - Retarding a potassium magnesium phosphate cement optionally containing flyash.

The formulation used in this example was as follows:

potassium carbonate	22g
10 mono ammonium phosphate	36g
(flyash)	25g
magnesium oxide	38g
and water	17ml

This formulation corresponds to a mole ratio of $\text{K}_2\text{CO}_3:\text{NH}_4\text{H}_2\text{PO}_4:\text{MgO}:\text{H}_2\text{O}$
15 of 1:2:6:6.

The mono ammonium phosphate was mixed with water and the potassium carbonate gradually added, with agitation to allow the CO_2 evolved in the reaction to escape. The mono ammonium phosphate and potassium carbonate particle size was $<500\mu\text{m}$. (Slight warming can be used at this stage to aid the further removal of CO_2
20 but intense heating is detrimental as it results in loss of ammonia). The mixing resulted in the formation of a white slurry (weighing ~70g). The magnesium oxide was then added to the slurry and stirred to form a smooth paste which could be cast after 1min, but also could be kept workable up to 15mins by continual agitation. If

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longer set times were required, water was added gradually, as stiffening occurred. A gradual addition of a further 10ml of water extended working time to 60mins. When the cement was made with flyash (added to the slurry prior to the addition of the magnesium oxide) then a further addition of 31ml of water extended workability to
5 60mins.

The foregoing describes only some aspects of the present invention and modifications made thereto without departing from the scope of the invention.

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CLAIMS

1. A method for slowing the setting rate of a magnesium phosphate cement comprising adding to a suitable base to an uncured or partially cured aqueous mix of the magnesium phosphate cement in an amount sufficient to raise the pH and
5 minimise MgO/Mg(OH)_2 dissolution.
2. A method according to claim 1 wherein the magnesium phosphate cement is an ammonium magnesium phosphate cement and the base is ammonia.
3. A method according to claim 1 wherein the magnesium phosphate cement is a potassium magnesium phosphate cement and the base is potassium hydroxide or
10 potassium carbonate.
4. A method of slowing the setting rate of an ammonium magnesium phosphate cement comprising the steps of reacting ammonia with an ammonium phosphate compound in the presence of water and subsequently reacting the mixture with a magnesium compound to form a compound having the formula $\text{NH}_4\text{MgPO}_4 \cdot n\text{H}_2\text{O}$,
15 wherein the amount of ammonia used is sufficient to raise the pH and minimise MgO/Mg(OH)_2 dissolution.
5. A method according to claim 4 wherein the ammonium compound is mono ammonium phosphate, and the magnesium compound is magnesium oxide.
6. A method of slowing the setting rate of potassium magnesium phosphate
20 cement comprising the steps of reacting an ammonium phosphate compound with a potassium compound in the presence of water and subsequently reacting the mixture with a magnesium compound to form a compound having the formula:



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wherein the amount of potassium compound used is sufficient to raise the pH and minimise MgO/Mg(OH)_2 dissolution.

7. A method according to claim 6 wherein the ammonium phosphate compound is mono ammonium phosphate, the potassium compound is potassium carbonate and
5 the magnesium compound is magnesium oxide.
8. A method according to any one of the preceding claims further comprising delaying the setting time by adding excess water and/or mechanically agitating the mix.
9. A method according to any one of the preceding claims wherein the cement
10 additionally contains fibres and/or fillers.

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00284

A. CLASSIFICATION OF SUBJECT MATTER

Int Cl⁶: C04B 9/04, 12/02, 22/06, 22/10, 28/30, 28/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC C04B 9/04, 12/02, 22/06, 22/10, 28/30, 28/34, 9/10, 17/03, 29/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
AU : IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DERWENT: (MAGNES:OR MG) (EXCEPT C04B 28/30:(PHOSPHAT:))
CHEM ABS: (MAGNES:OR MG) AND (PHOSPHAT:) AND (CEMENT:OR BIND:) AND (POTAS: OR K OR AMMON:)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DERWENT ABSTRACT Accession No. 78-33133 A/18, Class L02, JP 78-010094 A (MATSUSHITA ELEC WORKS) 11 April 1978 Abstract	1, 3, 8, 9
X	US 2, 522, 548 A (STREICHER) 19 September 1950 Column 6, line 42 - column 7, line 17 and column 11, line 56 - column 12, line 2	1, 3, 8, 9
X	PATENT ABSTRACTS OF JAPAN, C-843, page 118, JP 3-80137 A (NIPPON CHEM IND CO LTD) 4 April 1991 Abstract	1, 8, 9
Y	Abstract	3

☒ Further documents are listed in the continuation of Box C

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INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00284

C (Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PATENT ABSTRACTS OF JAPAN, C-843, page 118, JP 3-80138 A (NIPPON CHEM IND CO LTD) 4 April 1991 Abstract	3
X	DERWENT ABSTRACT Accession No. 80-54778 C/31, Class E33, L02, SU 694466 A (BELGOROD CONS MATER) 30 October 1979 Abstract	1, 3
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X	US 4, 444, 594 A (PADDISON et al.) 24 April 1984 Claims 2-4 and column 2, lines 45-49	1, 8, 9
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X	US 4, 436, 555 A (SUGAMA et al.) 13 March 1984 Claims 6 and 7	1, 8, 9
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X	EP 219, 952 A (STAUFFER CHEMICAL COMPANY) 29 April 1987 Column 9, lines 5-54 and column 12, lines 30-35	1, 2, 4, 5, 8, 9
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X	CHEMICAL ABSTRACTS, Volume 121, No. 18, 1994, Columbus, Ohio, U.S.A., A.K. SARKAR, "Investigation of reaction/bonding mechanisms in regular and retarded magnesium ammonium phosphate cement systems", page 433, column 1, the abstract no. 211501 U, Ceram. Trans. 1994, 40 (CEMENT TECHNOLOGY), pages 281-288 Pages 281-288	1, 8, 9

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00284

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	4, 444, 594	AT	4062/83	AU	17815/83	BE	897962
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		GB	2135986	JP	59-111962	LU	85097
		NL	8304233	SE	8304808		
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		GB	1512275	IT	1049911	JP	51-076320
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EP	219, 952	AR	240306	AU	31248/84	BR	8404034
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		DE	3678490	DE	3482319	DK	3872/84
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		ES	8607183	ES	545308	ES	8702319
		IL	74125	IN	161685	IN	166817
		JP	62-027365	JP	60-077154	KR	9203224
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		US	4755227	ZA	8405422		
AU	43473/85	CA	1241670	US	4836854		
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